

## Evaluation of Small Mass Spectrometer Systems

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### Abstract

This work is aimed at understanding the aspects of designing a miniature mass spectrometer (MS) system. A multitude of commercial and government sectors, such as the military, environmental agencies and industrial manufacturers of semiconductors, refrigerants, and petroleum products, would find a small, portable, rugged and reliable MS system beneficial.

Several types of small MS systems are evaluated and discussed, including linear quadrupole, quadrupole ion trap, time of flight and sector. The performance of each system in terms of accuracy, precision, limits of detection, response time, recovery time, scan rate, volume and weight is assessed. A performance scale is setup to rank each systems and an overall performance score is given to each system.

All experiments involved the analysis of hydrogen, helium, oxygen and argon in a nitrogen background with the concentrations of the components of interest ranging from 0 – 5000 part-per-million (ppm). The relative accuracies of the systems vary from < 1% to ~40% with an average below 10%. Relative precisions varied from 1% to 20%, with an average below 5%. The detection limits had a large distribution, ranging from 0.2 to 170 ppm. The systems had a diverse response time ranging from 4 s to 210 s as did the recovery time with a 6 s to 210 s distribution. Most instruments had scan times near, 1 s, however one instrument exceeded 13 s. System weights varied from 9 to 52 kg and sizes from  $15 \times 10^3 \text{ cm}^3$  to  $110 \times 10^3 \text{ cm}^3$ .

## Introduction

There is an ever-increasing need for smaller mass spectrometer (MS) systems. Compared to current commercial systems, small MS systems are generally more easily transported, less expensive, operated in more diverse environments, and allow real-time analysis. Such systems have many potential applications such as environmental analysis, process monitoring, leak detection and hazardous chemical detection. At Kennedy Space Center there is a need for small, point-sensor MS systems for a variety of tasks. Such tasks include the monitoring of hazardous gases around the Space Shuttle prior to launch, the detection of toxic vapors, such as hypergols, and process control of a fuel production plant on Mars.

Mass spectrometer systems have been used since the beginning of the space program [1]. The primary reason mass spectrometers are used is due to their excellent limits-of-detection, response time, recovery rate, accuracy and capability to monitor and differentiate several species. One aspect of the work at Kennedy Space Center is to develop systems that monitor the cryogenic fuels, liquid hydrogen and liquid oxygen, used for launching the Space Shuttle. A build up of gaseous hydrogen or oxygen during fueling or launch creates a hazardous environment. For this reason, areas of potential hazard are purged with nitrogen and analyzed for hydrogen, helium, oxygen and argon. [Hydrogen and oxygen indicate a leak of the cryogenics, argon indicates a leak to air and helium is used for leak checking prior to fueling.]

Currently a large mass spectrometry system [2, 3] performs this task, using long transport lines to draw in samples from various points around the Shuttle. This arrangement is depicted in Figure 1. The current system has several undesirable attributes. Since the sampling points are removed from the MS system, long transport lines (up to 370 ft) are used. As a result, the sample being analyzed is actually 15 – 30 s old. Among the various problems arising from the delay, monitoring the last fraction of a minute prior to launch is precluded. The sequential, round-robin sampling of the lines also causes delay difficulties. This system is also very large ( $\sim 3.65 \times 10^6 \text{ cm}^3$ ), heavy ( $\sim 1700 \text{ lbs.}$ ) and expensive ( $\sim \$1\text{M}$ ). Lastly, if more sampling points were added, more transport lines would be needed, adding to the size and weight, and there would be an even longer delay between consecutive readings due to the round-robin scanning method.

There is great interest in replacing this stationary system with several miniature [4], portable, rugged mass spectrometers to act as point sensors, which can be placed at the sampling locations. Small, lightweight systems would provide several advantages. First, being a point sensor there is no need for the long transport lines, thus eliminating the delay between sample uptake and analysis. Second, with multiple sensors, monitoring of several locations can be performed simultaneously. Additional sampling points would not create a delay between consecutive scans. Third, small instruments tend to cost less than their larger counter-parts. Fourth, in the event one system fails, several entire systems could be on the shelf ready for installation. Currently, when an instrument fails that instrument is evaluated and the part(s) are repaired or replaced. This requires the stocking of several parts, and technician repair time. Also, with the systems being lightweight and portable there is the potential that these systems can remain functional during the launch, ascent, orbit and descent.

In order to achieve this goal, such a miniature MS system should have the following properties. First, the system must be small ( $< 35,000 \text{ cm}^3$ ), lightweight ( $< 10 \text{ kg}$ ), power efficient ( $< 250 \text{ W}$ ), rugged (survive 18 g), and relatively inexpensive ( $\sim \$20,000$ ). The system should also have low limits-of-detection ( $\sim 10 \text{ ppm}$ ), fast response and recovery times ( $\sim 30 \text{ s}$ ),

rapid scan time ( $\sim 1$  s) and provide accurate results ( $< 10\%$  error) over a sustained period of time ( $\sim 12$  hours).

Eight small mass spectrometer systems were evaluated for air analysis. Hydrogen, helium, oxygen and argon were measured at low levels, 100 – 5000 ppm, in a nitrogen background. Under these conditions, the various performance parameters were determined.

## Experimental

The eight instruments evaluated can be organized into three categories: system involved in the Small Business Innovative Research (SBIR) grant program, commercial off-the-shelf (COTS) instruments, and in-house developed systems. Table 1 summarizes the instruments, models and analyzer types of the systems evaluated. Note that the Ferran, IonWerks, MG-2100 and Polaris-Q are complete systems. The SRS, and XPR-2 are only analyzers, the rest of the systems were built in-house.

Table 1  
Systems Used

System Type	Manufacturer / Model	Analyzer Type
SBIR	Ferran	Linear Quadrupole Array
	IonWerks (TOF)	o-TOF
COTS	Stanford Research Systems RGA-100 (SRS)	Linear Quadrupole
	Inficon XPR-2	Linear Quadrupole
	Monitor Instruments MG-2100	Cycloidal Focus
	Thermo Finnigan Polaris Q	Quadrupole Ion Trap
In-House	University of Florida/KSC (UF-IT)	Quadrupole Ion Trap
	University of Minnesota/KSC (CDFMS)	Double Focus Sector

The Ferran [6 – 9] system utilizes a miniature linear quadrupole array consisting of 16 rods. Each rod has a diameter of 1mm and a length of 10 mm. The operating frequency for this system is 16 MHz and a Faraday cup is used for detection. The IonWerks Time-of-Flight (TOF) is an orthogonally accelerated reflectron. A unique anode detector is used, which is claimed to increase the dynamic range [10]. The Stanford Research Systems RGA-100 is a linear quadrupole system with rod diameters of 0.25" and length of 4.5". The operating frequency is 2.7648 MHz and both a Faraday cup and electron multiplier detectors are available, although the multiplier is used here. For this application, the system operates best when the analyzer is in the mid- $10^{-5}$  Torr pressure range. The Inficon XPR-2 is a linear quadrupole system with hyperbolic rods with an inscribed radius of 0.013" and length of 0.5". The XPR-2 operates at 13 MHz and has both a Faraday cup and channel electron multiplier detectors. This system generally operates with the electron multiplier and an analyzer pressure in the low  $10^{-4}$  Torr range. The Monitor Instruments MG-2100 is a cycloidal focusing sector. The ThermoQuest Polaris-Q is a quadrupole ion trap of stretched geometry with an internal ring radius of 7 mm and operating at a frequency of 1.03 MHz. Due to the geometry and operating frequency, the Polaris-Q is unable to monitor hydrogen and helium. The compact double focusing sector (CDFMS) is a crossed electric and magnetic field sector analyzer with a  $90^\circ$  geometry that was developed at the University of Minnesota [11 – 14]. The magnetic field strength was 0.75 T and the sector radius was 2 cm. A second quadrupole ion trap, the UF-IT, was developed at the University of Florida

[15, 16]. This ion trap is of stretched geometry with an internal ring radius of 10 mm and operates at a frequency of 2.9 MHz.

With the exceptions of the UF-IT, Polaris-Q and TOF, all instruments used an Alcatel ATH 30+ turbomolecular-drag high vacuum pump. This pump was chosen due to its high compression ratios for hydrogen and helium, as well as nitrogen ( $10^5$ ,  $10^7$  and  $10^{11}$ , respectively). The high compression ratios are needed for good response and recovery times between samples. The TOF has a Varian V70LP high vacuum turbomolecular pump; the UF-IT uses a Pfeiffer model TPH-65 turbomolecular-drag pump and the Polaris-Q use a Edwards model 70H turbomolecular-drag pump. In order to maintain clean vacuum chambers and mass analyzers, either scroll pumps or diaphragm pumps are used for backing the turbomolecular pumps and for providing sample delivery. In general, a Varian 300 Scroll pump is used for sample delivery, and typically a diaphragm pump is used with the turbo pumps. All systems use electron impact (EI) ionization with thoriated iridium filaments operating at 70 eV.

A similar experiment is used to evaluate all mass spectrometers. The experimental sequence is depicted in Figure 2. A zero bottle (> 99.995% N<sub>2</sub>), test bottle (500 ppm H<sub>2</sub>, 500 ppm He, 500 ppm O<sub>2</sub>, 100 ppm Ar and balance N<sub>2</sub>, nominally) and span bottle (5000 ppm H<sub>2</sub>, 5000 ppm He, 5000 ppm O<sub>2</sub>, 1000 ppm Ar and balance N<sub>2</sub>, nominally) are analyzed sequentially for approximately 5 minutes each. This cycle constitutes the calibration cycle, where the zero and span serve as a two-point calibration curve and the test is used to determine the quality of the calibration. All data values are determined using a 10-point data set. Following the calibration cycle, the test bottle, is analyzed for 5 minutes and then returned to the zero bottle. At this time, the calibration cycle is used to scale all data in terms of concentration with which the parameters of evaluation are determined.

With the various definitions available for the parameters used in this study, each parameter is defined below. Accuracy, Equation 1, is the ratio of the difference between the measured test concentration and the true concentration to the true concentration. When shown

$$A = \frac{[test]_{meas} - [test]_{true}}{[test]_{true}} \times 100\% \quad (1)$$

graphically, accuracy is reported as its absolute value. Precision, Equation 2, is the ratio of the standard deviation of the measured data set for the test bottle to the measured concentration

$$P = \frac{\sigma_{meas}}{[test]_{meas}} \times 100\% \quad (2)$$

of the test bottle. As described in Equation 3, the theoretical limit of detection (LOD) is defined as 3 times the standard deviation of the zero data set. Response time is the time between the

$$LOD = 3 \times \sigma_{zero} \quad (3)$$

bottle change from zero gas to test gas until the reading is within 95% of the average measured test value. The recovery time is the elapsed time between changing the bottle from the test gas to the zero gas and a signal reading 5% of the test reading (95% reduction in signal). Scan time is the time required for one scan to be acquired and the data to be transferred. It is determined by

measuring the time required acquiring a known number of scans and dividing by said number of scans. The system volume is determined by measuring the entire system volume including the mass analyzer, its associated electronics, vacuum system, high vacuum pump and rough pump. Also measured are any ion gauge controllers or other required equipment. Computers are not included. System weight is determined by weighing each individual component – again computers are not included. These evaluation parameters along with the defined requirements are summarized in Table 2.

Table 2  
Summary of Experimental Parameters [17]

Parameters	Definition	Shuttle Requirements
Accuracy	$\frac{[Test]_{meas} - [Test]_{true}}{[Test]_{true}} \times 100\%$	< 10% or 5ppm, which ever is greater
Precision	$\frac{\sigma_{Test, meas}}{[Test]_{meas}} \times 100\%$	< 5% or 3ppm, which ever is greater
Limit of Detection	$3 \sigma_{zero}^{(1)}$	H <sub>2</sub> , O <sub>2</sub> : 25 ppm; He: 100 ppm; Ar: 10 ppm <sup>(2)</sup>
Response Time	Time required for response from valve change to 5% new reading	10 s
Recovery Time	Time after valve change to reach 5% of previous sample reading (new sample is zero)	30 s
Scan Time	Experiment Time / Scans	1 s
Maximum Size	Sum of Individual Components	$3.5 \times 10^4 \text{ cm}^3$
Maximum Weight	Sum of Individual Components	10 kg

<sup>(1)</sup> Theoretical Limit of Detection, <sup>(2)</sup> Measured Limit of Detection

## Results & Discussion

Although an accuracy requirement of 10% may seem trivial among analytical techniques, when using a MS to analyze permanent gases from part-per-million to the sub-percent range this is typical. Figure 3 shows the results of the accuracy tests for each system and component evaluated. Half of the systems (SRS, XPR-2, UF-IT, and CDFMS) met the required (< 10%) accuracy. Of the remaining systems, the Polaris-Q slightly exceeds the requirements for argon with an accuracy of 13%. The accuracies of the Ferran, TOF and MG-2100 were greater than 10% for many of the analyzed components; this is considered unacceptable.

It is important to point out that there are no clear trends with each component in regards to accuracy. For example, hydrogen is very difficult to analyze using a linear quadrupole due to the zero-blast and the very shallow pseudo-potential well [18]. But, in the case of the SRS, hydrogen has the best accuracy of all of the components, yet in the case of the XPR-2, it is nearly the worst.

Figure 4 displays the precision results for the various systems and for each component analyzed. Half of the systems (SRS, Polaris-Q, UF-IT and CDFMS) meet the requirements with the TOF slightly exceeding. The MG-2100 mildly exceeds the requirements, while the XPR-2

and Ferran have significant precision problems with precisions exceeding 15%. The SRS, Polaris-Q and UF-IT systems are substantially better than the required 5% precision level.

It is not clear what factors affect precision but several components are suspected. For example, it is believed that maintaining a stable pressure at the sample inlet is of primary importance. All of the systems evaluated here maintained a stable pressure via in-house sample delivery system (SDS). The sample delivered to the MS is drawn downstream of an manual needle valve (to maintain a desired flow rate) and upstream of the pressure transducer and flow controller. The pressure transducer and flow controller are used in combination to control the upstream pressure. We have found that using this configuration, controlling the pressure in an upstream (rather than downstream) manner, provides better response time to changes in the sample. It is believed that the method by which the sample is introduced into the MS can affect the precision. Three techniques are used here. The SRS, XPR-2, Polaris-Q and UF-IT use orifices for sample introduction. The Ferran, TOF and MG-2100 use capillaries, and the CDFMS uses a frit for sample introduction. More often than not, the orifice technique provides better results. Also, the pressure within the analyzer may affect the precision. The SRS, UF-IT, TOF, MG-2100 and CDFMS all operate in the  $10^{-5}$  Torr range. The XPR-2 and Ferran operate in the  $10^{-4}$  Torr range and the Polaris-Q operates in the upper  $10^{-4}$  (and lower  $10^{-3}$ ) Torr range. No clear trend has been observed that indicates what operating range is best for precision purposes, yet each system has a very specific pressure range in which optimum performance is found.

The limits of detection (LOD) for each instrument are shown in Figure 5. The best instrument for LOD is the SRS, while the XPR-2 also performs within specifications. As far as detecting  $O_2$  and Ar, the Polaris-Q performed very well, but its mass range prevented it from detecting  $H_2$  and He. With the exception of detecting oxygen, the UF-IT performed quite well in this category. The Ferran performed well for Ar, but needs significant improvement in detection of  $H_2$  and  $O_2$ . Although it appears that the Ferran performs well for He, but this is an artifact of the LOD calculation. The data analysis software of the Ferran imposes an ion current threshold. An ion current lower than the threshold is assigned a value of zero. As a result, the analysis of helium in the zero gas results in a data set with mostly zeros, thus artificially lowering the LOD. The TOF, MG-2100 and the CDFMS need significant improvement for all of the gases.

The LOD is one of the more challenging specifications to meet or exceed. There are a variety of reasons for this. An important factor in analyzing these gases is their high ionization potentials ( $H_2$ : 15.4 eV, He: 24.6 eV,  $N_2$ : 15.6 eV,  $O_2$ : 12.1 eV, Ar: 15.8 eV). As a result the ionization efficiency tends to be low relative to the typical volatile organic. Preconcentration of the analyte through GC, as is commonly done with volatile organics to achieve ppb LODs, is not viable here due to time per scan considerations. Preconcentration via removal of the “carrier gas”, nitrogen in this case, is another technique to improve LOD. Achieved using a gas jet separator, this works quite well for components of mass greater than the carrier gas since jet separators act as high pass (passing masses higher than the carrier) filters. Unfortunately, this would significantly hinder hydrogen and helium analysis.

Response times for each system (and respective components) are shown in Figure 6. With a specification of 10 s, the SRS and UF-IT meet the requirements. Only hydrogen exceeds the 10 s mark for the XPR-2. Although the Polaris-Q response times are higher than desired, they are still in a reasonable range. Unfortunately, the Ferran, TOF, MG-2100 and CDFMS exceed the requirements by a factor of 3 or more. Based on fluid dynamics, one would expect

the response times to decrease as a function of molecular mass, but no such general trend is observed.

Figure 7 displays the recovery times for each MS system. The XPR-2, UF-IT and MG-2100 meet the requirement of 30 s. A few of the analyzed components exceed the specifications for the SRS and CDFMS, but in general these systems are deemed adequate. All components for the Polaris-Q and TOF exceed the specifications by a factor of 2, which demonstrates a strong need for improvement. And, the Ferran has components with response times in excess of 3 minutes, which is entirely unacceptable. Again, one would predict lower recovery times for heavier components, but no such trend is observed.

One of the most important parameters that affect response and recovery time is dead volume prior to sample introduction. For the systems built in-house, great care was taken to reduce any unnecessary dead volume by placing the sample inlet as close as possible to the SDS. Also, appropriate diameter and length tubing was used so as to reduce dead volume while minimizing unwanted pressure reduction. Another parameter affecting response and recovery time is the flow rate of the sample gas past the sample inlet – a higher flow rate is generally better. The flow rate of the sample past the sample inlet varied from system to system. Typical values are approximately 10 – 50 sccm (standard cubic centimeters per minute). Although the actual flow rate varied at the point of sample introduction, a constant flow rate (350 sccm) was maintained at the SDS for all systems evaluated.

Figure 8 illustrates the scan time for each of the systems under study. Most of the systems have a scan time less than the 2 second requirement. The SRS, Ferran and MG-2100 significantly exceed the requirements. The scan times for the SRS and Ferran can be reduced, but this is very detrimental to the limits-of-detection and other parameters.

The volume for each system is shown in Figure 9. For reference purposes, an Alcatel ATH 30+ turbo pump has a volume of 1200 cm<sup>3</sup>. The most space efficient systems, the XPR-2 and the CDFMS are those that can operate using smaller backing pumps. The Ferran represents an acceptable volume. The largest system is the Polaris-Q. The primary bulk of the Polaris-Q arises from the electronics and rough pump, however one should note that this system was designed to be a bench top system. The second least space efficient system, the TOF, actually has a small mass analyzer, but the electronics account for the bulk. The SRS volume is too high primarily due to the required rough pump and the length of the quadrupole rods. The UF-IT volume is inefficient primarily as a result of its in-house construction status. It is interesting to note that the smallest system was one built in-house, even though three of the commercial systems (Ferran, TOF and MG-2100) are specifically marketed, or will be marketed, as miniature MS systems.

In viewing the literature, one would think that analyzer size and performance are the major issues of miniaturization. Analyzer technology is sufficiently mature and the size is small enough that these are secondary issues. But, as can be seen in Figure 9, the primary concerns in reducing the size of the systems are the pump size [19] and the electronics.

System weight is one of the more challenging requirements to meet. Large portions of these systems are generally constructed of some form of steel – the vacuum chamber, the rough pump, the turbo pump and typically the frame. As a result only one of the systems evaluated (CDFMS) met the required 10 kg (22 lbs) limit. Figure 10 compares the overall weights of the each of the systems as well as a breakdown of the subsystems. Similar to the volume analysis, the rough pump and electronics account for the majority of the weight of each system.

Although not quantifiable as a specific parameter, there are other aspects of the systems that should be mentioned. For example, the Ferran and MG-2100 have undesirable sample inlet systems. The Ferran has a direct inlet system, using a capillary for pressure reduction. Although this method does provide the needed pressure reduction for the MS, it has the tendency to increase the response and recovery times. The MG-2100 also uses a capillary inlet for pressure reduction, although this system is not a direct inlet system. Instead, the MG-2100 has a “flow-by” [20] stage to reduce the pressure while maintaining an acceptable flow rate. Two problems are associated with the MG-2100 inlet design; first the capillary protrudes beyond the fitting, allowing the capillary to be broken on occasion. Also, even though the flow-by technique is superior for response and recovery times, the use of a capillary still deteriorates these times, relative to the use of an orifice. The Ferran had significant communication problems. This system was designed to be RS-232 compatible, yet communication errors would occur much too often (up to 50% downtime as a result). This represents an important reliability concern. The time-of-flight had problems with its electronics. On at least two occasions within six months, an unregulated power supply failed. The Polaris-Q is unable to analyze hydrogen and helium, which is vital for the application mentioned above. Although this was known from the beginning of the study, the evaluation of the Polaris-Q assisted in the design of the UF-IT, and demonstrated the capabilities of a commercial ion trap. The ion trap is of great interest due to its inherent ion manipulation and MS<sup>n</sup> capabilities [21].

It is difficult to determine which system is best considering all of the factors involved. A somewhat arbitrary method was used. Each system was given a ranking number between 1 and 10 for each of the evaluation parameters. With 1 being excellent, 5 being just within specification, and 10 being unacceptable, the categories are averaged to result in a final evaluation score for each system. The systems considered acceptable (a score of < 5.1) are the

Table 3  
Total Ranking of Evaluated Systems

	Accuracy	Precision	LOD	Response	Recovery	Scan Rate	System Volume	System Weight	Score
SRS	2	2	1	2	6	8	6	7	<b>4.3</b>
XPR-2	3	8	2	7	5	5	2	6	<b>4.8</b>
Ferran	10	10	7	10	10	9	3	6	<b>8.1</b>
Polaris-Q	7	3	2	8	8	2	10	10	<b>6.3</b>
UF-IT	3	3	6	3	3	2	7	8	<b>4.4</b>
TOF	9	6	7	9	7	2	9	8	<b>7.1</b>
MG-2100	9	7	10	10	5	10	6	7	<b>8.0</b>
CDFMS	4	5	9	8	6	2	2	4	<b>5.0</b>
<b>Average</b>	<b>5.9</b>	<b>5.5</b>	<b>5.5</b>	<b>7.1</b>	<b>6.3</b>	<b>5.0</b>	<b>5.6</b>	<b>7.0</b>	

SRS, XPR-2, UF-IT and the CDFMS with scores of 4.3, 4.8, 4.4 and 5.0, respectively. Ideally these four systems would have scores in the 2 – 3 range indicating an instrument that performs well in most, if not all, categories. With scores in the 4 – 5 range suggests that although these systems are close to meeting the requirements, there is still much improvement needed. In order to determine which parameters need improvement, an average for each criterion was taken (the



last row in Table 3). According to the average, only the scan rate is reasonable. The parameters that need the most attention appear to be the response time and system weight, with averages of 7.1 and 7.0 respectively. Although evaluating the instruments as shown in Table 3 is somewhat arbitrary, it at least provides a guide as to which instruments are worth spending time and money on improving and which parameters need the most attention.

## Conclusions

A cross section of small mass spectrometer systems were evaluated, with analyzers such as linear quadrupole, quadrupole ion trap, time-of-flight, and sector. These systems were evaluated for the purpose of developing miniature systems for gas detection around the Space Shuttle. Many parameters were evaluated including the measurement accuracy and precision, limit-of-detection, response and recovery times, system volume and weight. The systems that were determined to work best include a linear quadrupole from Stanford Research Systems (SRS RGA-100), a miniature linear quadrupole from Inficon (XPR-2), an in-house built quadrupole ion trap and an in-house built double focusing sector. No system met all the requirements set forth, but with research and modifications to these instruments it is believed that a miniature MS system that is capable of rapid, reliable, accurate and precise analysis is close at hand.

Future work will be focused in several areas. Limits of detection, along with accuracy and precision improvements will be addressed through the investigation of new sample introduction techniques, ionization conditions and ion focusing. Improvements in response and recovery times are being addressed with sample introduction and gas pumping methods. Investigation into new pump technology is being used to reduce system volume and weight. As the need for miniature MS systems grows and more researchers enter the field, the time is quickly approaching when a viable miniature system is developed.

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[1] For a review of instruments used with the Shuttle see:

(a) Palmer, P. T.; Limero, T. F. "Mass Spectrometry in the U.S. Space Program: Past, Present and Future", *J. Am. Soc. Mass Spectrom.*, **2001**, 12, 656-675. (b) Helms, W. R. "History, Design and Performance of the Space Shuttle Hazardous Gas Detection System", Space Shuttle Technical Conference, Houston, TX, 1983, NASA Conference Publication 2342, Part 1, 573-580. (c) Helms, W. R., Raby, B. A. "A Prototype Hazardous Gas Detection System for NASA's Space Shuttle", The 26th ASMS Conference On Mass Spectrometry And Allied Topics, St. Louis, MO, **1978**, 463-5.

[2] T. P. Griffin, G. R. Naylor and W. D. Haskell; G. S. Breznik and C. A. Mizell, "A Fully Redundant On-Line Mass Spectrometric System for the Space Shuttle Used to Monitor Cyogenic Fuel Leaks", 2nd Workshop on Harsh-Environment Mass Spectrometry, March 18-21, 2001, St. Petersburg, FL.

[3] Mizell, C. A.; Griffin, T. P.; Naylor, G. R.; Haskell, W. D.; Hritz, R. J. "Hazardous Gas Detection System", Research and Technology 2000/2001, NASA Technical Memorandum 210258. (Also available at [http://technology.ksc.nasa.gov/WWWaccess/R&T\\_reports.html](http://technology.ksc.nasa.gov/WWWaccess/R&T_reports.html))

[4] For review of miniature mass analyzers see:

Badman, E. R.; Cooks, R. G. "Miniature Mass Analyzers", *J. Mass Spectrom.*, **2000**, 35, 659-671.

- [5] Arkin, C R.; Ottens, A. K.; Diaz, J. A.; Griffin, T. P.; Follistein, D.; Adams, F.; Helms, W. R. "Evaluating Mass Analyzers as Candidates for Small, Inexpensive, Rugged Single Point Mass Spectrometers for Analysis of Permanent Gases." Proceedings of the 49th ASMS Conference On Mass Spectrometry And Allied Topics, Chicago, IL, 2001.
- [6] Boumsellek, S.; Ferran, R. J. "Trade-offs in Miniature Quadrupole Designs", *J. Am. Soc. Mass Spectrom.*, **2001**, 12, 633-640.
- [7] Ferran, R. J. U.S. Patent. "Residual gas sensor utilizing a miniature quadrupole array", 28 March 1995, 5,401,962.
- [8] Ferran, R. J. U.S. Patent. "Residual gas sensor utilizing a miniature quadrupole array", 12 January 1999, 5,857,890.
- [9] Ferran, R. J.; Boumsellek, S. "High-pressure effects in miniature arrays of quadrupole analyzers for residual gas analysis from  $10^{-9}$  to  $10^{-2}$  Torr", *J. Vac. Sci. Technol. A*, **1996**, 14, 1258-1265.
- [10] Gonin, M.; Fuhrer, K.; Schultz, A. "A New Concept to Increase Dynamic Range using Multi-Anode Detectors", Proceedings of the 48th ASMS Conference On Mass Spectrometry And Allied Topics, Long Beach, CA, **2000**, 326-327.
- [11] Diaz, J. A.; Giese, C. F.; Gentry, W. R. "Sub-Miniature ExB Sector-Field Mass Spectrometer", *J. Am. Soc. Mass Spectrom.*, **2001**, 12, 619-632.
- [12] Diaz, J. A. "Design, modeling and process of a micro-fabricated mass spectrometer on a chip for analytical applications." MSEE Thesis. University of Minnesota, 1998.
- [13] Diaz, J. A. "Sub-miniature double-focusing mass spectrometer for in-situ environmental monitoring and application to volcanic gaseous emissions." Ph.D. Thesis. University of Minnesota, 1999.
- [14] Diaz, J. A.; Gentry, W. R.; Giese, C. F. Patent Application, University of Minnesota, 96035, 1999.
- [15] Ottens, A. K.; Griffin, T. P.; Yost, R. A. "A Quadrupole Ion Trap Mass Spectrometer for Quantitative Analysis of Nitrogen-Purged Compartments within the Space Shuttle." The 49th ASMS Conference On Mass Spectrometry And Allied Topics, Chicago, IL, 2001.
- [16] Ottens, A. K.; Harrison, W. W.; Griffin, T. P.; Helms, W. R. "", *J. Am. Soc. Mass Spectrom.*, **2002**, submitted.
- [17] Griffin, T. P. "Advanced Hazardous Gas Detection System (AHGDS) (Design Decisions), Requirements Document", KSC-MM-4864, 10 Jan 2001.
- [18] P. H. Dawson, Quadrupole Mass Spectrometry and its Applications. Elsevier, Amsterdam, 1976.
- [19] 1999 NASA/JPL Miniature Vacuum Pumps Workshop, Glendale, CA, July 20-21, 1999.
- [20] The term "flow-by" is used to describe a sampling technique in which the sampling entrance is orthogonal to the primary gas flow.
- [21] March, R. E. "An Introduction to Quadrupole Ion Trap Mass Spectrometry", *J. Mass Spectrom.*, **1997**, 32, 351-369.

## Figure Captions

### Figure 1: Location of Current Instrument and Sample Positions

The current gas detection system, HGDS 2000, is located in the mobile launch platform (MLP). As a result the samples must be transported from around the launch vehicle to the detection system. The HGDS 2000 system is depicted by the black square with the 5 sample lines attached. The approximate positions of the 5 sample locations are shown and are the 1) external tank-internal tank, 387ft. 2) midbody, 227 ft. 3) payload bay, 226 ft. 4) hydrogen side umbilical, 209 ft. and 5) aft, 200 ft.

### Figure 2: Example of Typical Evaluation Experiment

The general experiment used to evaluate the mass spectrometers begins with a calibration cycle. This cycle uses a zero bottle ( $> 99.995\% \text{ N}_2$ ), test bottle (500 ppm  $\text{H}_2$ , 500 ppm He, 500 ppm  $\text{O}_2$ , 100 ppm Ar and balance  $\text{N}_2$ , nominally) and span bottle (5000 ppm  $\text{H}_2$ , 5000 ppm He, 5000 ppm  $\text{O}_2$ , 1000 ppm Ar and balance  $\text{N}_2$ , nominally) where each is analyzed for 5 minutes sequentially. The zero and span serve as a two-point calibration curve and the test is used to determine the quality of the calibration. Following the calibration cycle, the test bottle is analyzed for 5 minutes then returning to the zero bottle. This allows for the other test parameters to be determined as described in the text.

### Figure 3: Comparison of the Accuracy of each Instrument for each Species

The accuracy is determined by comparing the true concentration of the test gas to that measured and reported in terms of absolute values. At these concentration levels, an error of 10% or less is acceptable.

### Figure 4: Comparison of the Precision of each Instrument for each Species

The precision is the ratio of the standard deviation of the test gas measurement to the average of the test gas measurement. At these concentration levels, a 5% precision level or less is acceptable.

### Figure 5: Comparison of the Theoretical Limits of Detection (LOD) of each Instrument for each Species

The theoretical LOD is calculated to be three times the standard deviation of the zero gas measurement. The required, measured LODs are given in Table 2.

### Figure 6: Comparison of the Response Times of each Instrument for each Species

Response times are measured as the time between when the zero to test bottle change occurs until the measured concentration is within 95% of the average measured concentration of the test gas. An acceptable response time is 10 seconds or less.

### Figure 7: Comparison of the Recovery Times of each Instrument for each Species

The recovery time is measured as the time between when the test to zero bottle change occurs until the measured concentration is 5% of the average measured concentration of the test gas. An acceptable recovery time is 30 seconds or less.

Figure 8: Comparison of the Scan Times for each Instrument

The required time to measure all four gases of interest in a selected ion-monitoring mode. Two seconds or less is considered an acceptable scan time.

Figure 9: Comparison of the Volume of each System

The volume of the systems, less the controlling computer and the sample delivery system, are illustrated and categorized into four sub-systems: the analyzer and vacuum system, the electronics, the turbo pump, and the backing pump. A volume of 35,000 cm<sup>3</sup> or less is acceptable [Since the Polaris-Q, Ferran and MG-2100 are integrated products, it is difficult to separate the volume used by the electronics and that of the other components. Since electronics are generally placed in the remaining open spaces allowed by the pumps and chamber, the volume of the electronics and vacuum system were considered the same.]

Figure 10: Comparison of the Weight of each System

The weight of the systems, less the controlling computer and the sample delivery system, are illustrated and categorized into four sub-systems: the analyzer/vacuum system/frame, the electronics, the turbo pump, and the backing pump. A weight of less than 10 kg is desired. [Since the Polaris-Q, Ferran and MG-2100 are integrated products, it is difficult to separate the weight of the electronics and that of the other components. As a result, the weight of the electronics and vacuum system were considered the same.]

Figure 1  
Location of Systems

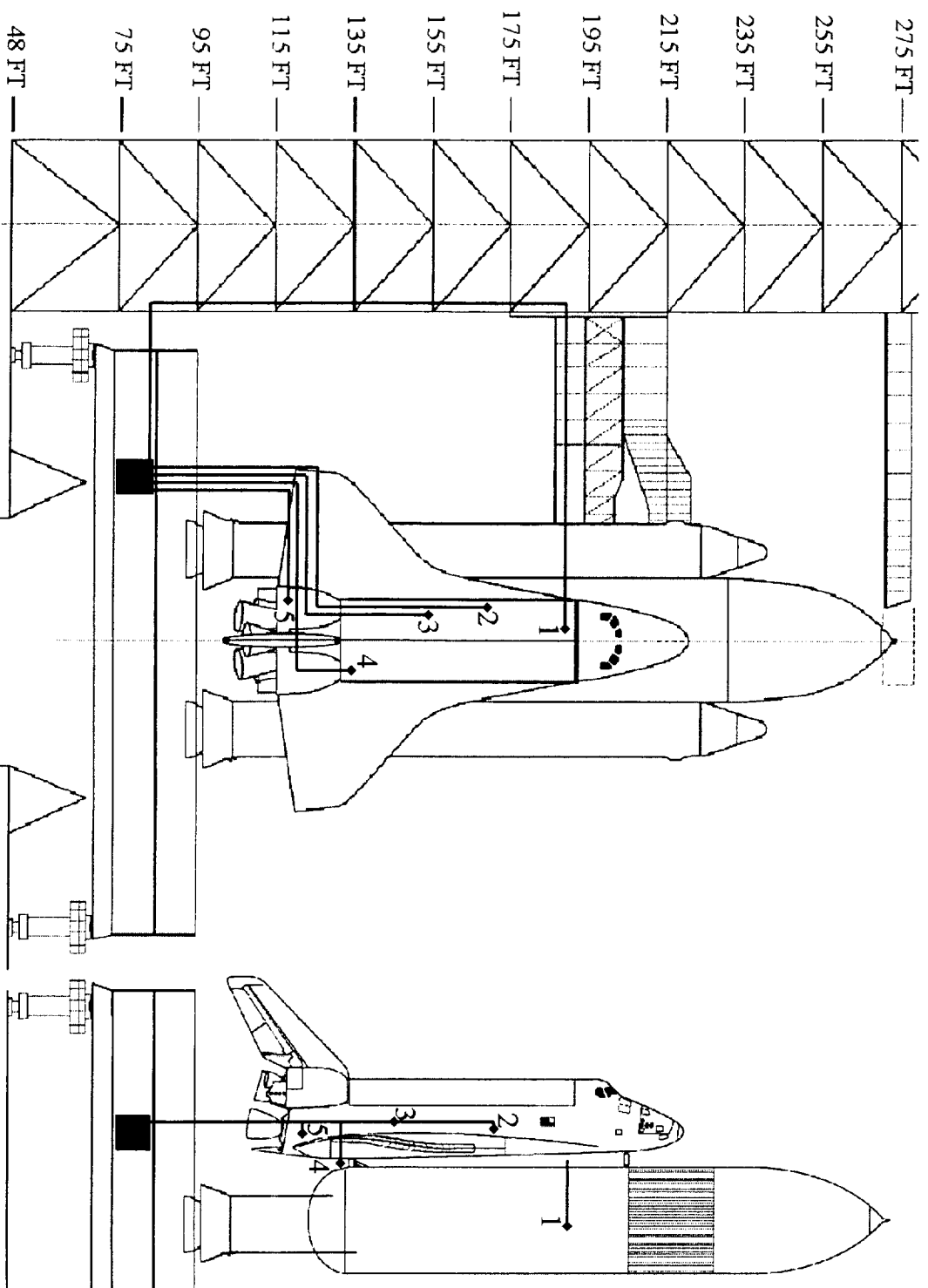
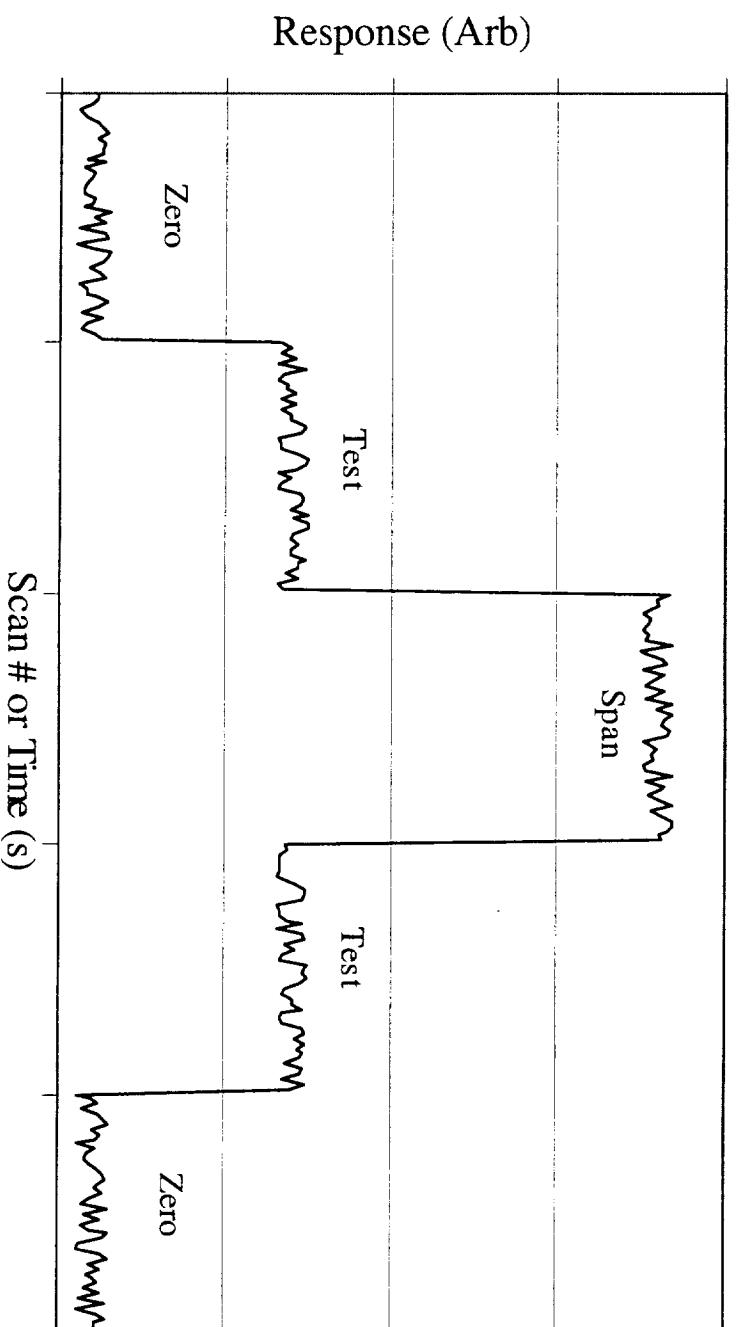


Figure 2  
Example of a Typical Experiment



# Figure 3

## Accuracy

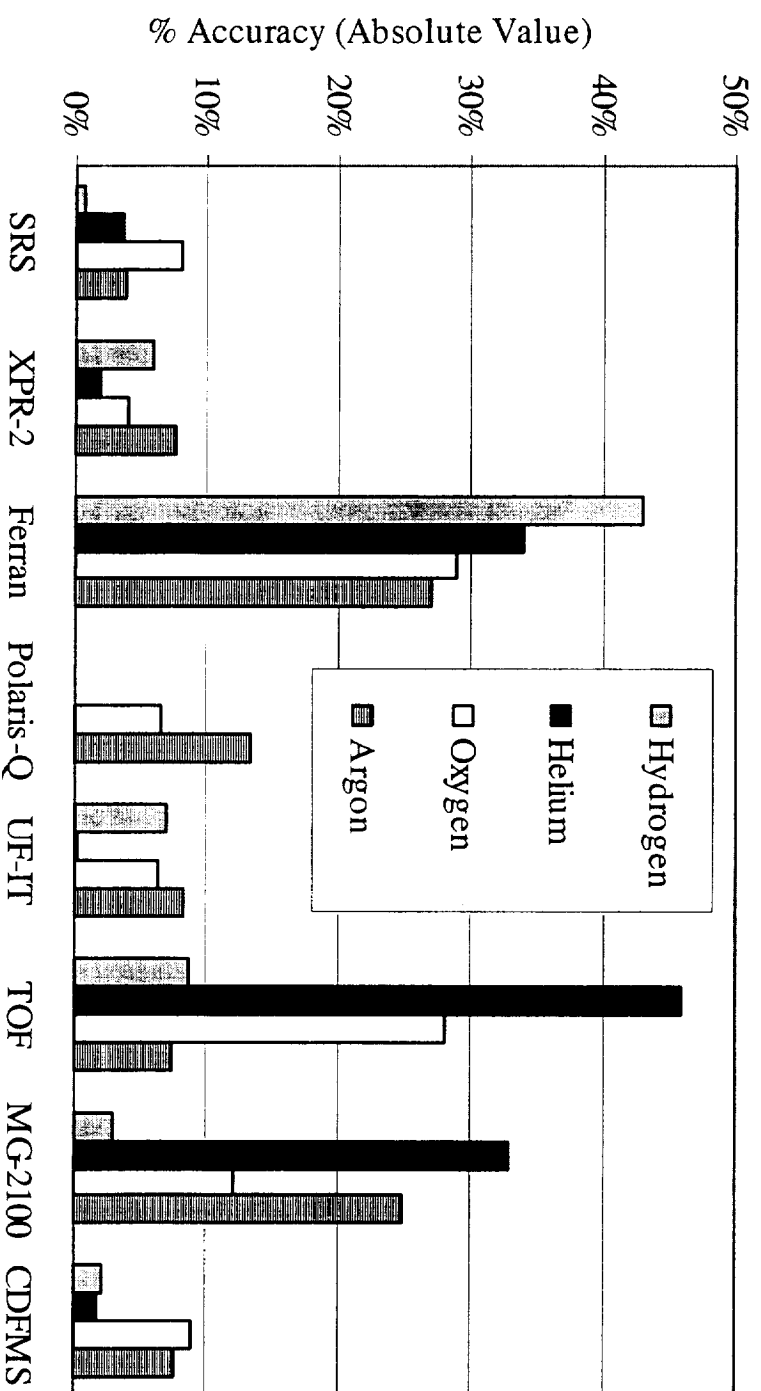
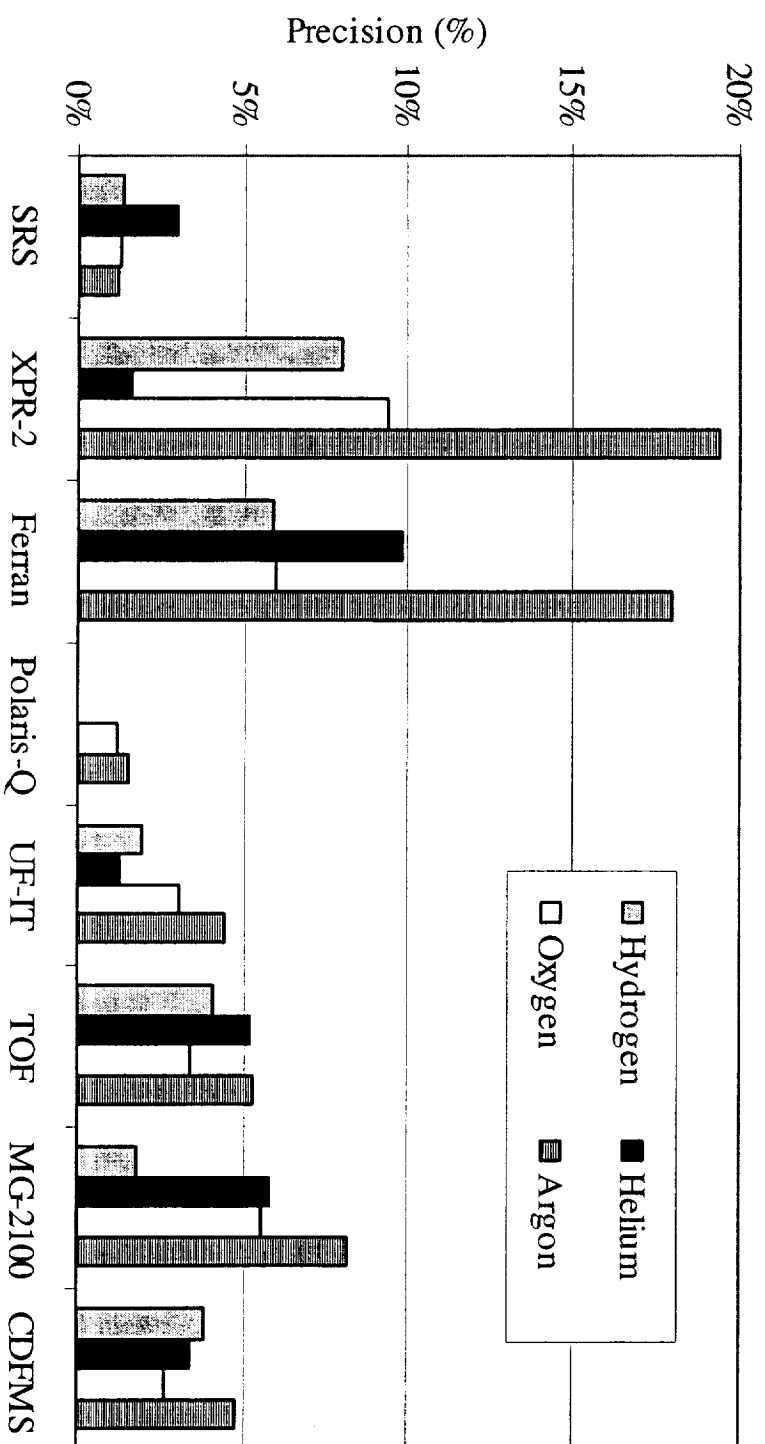


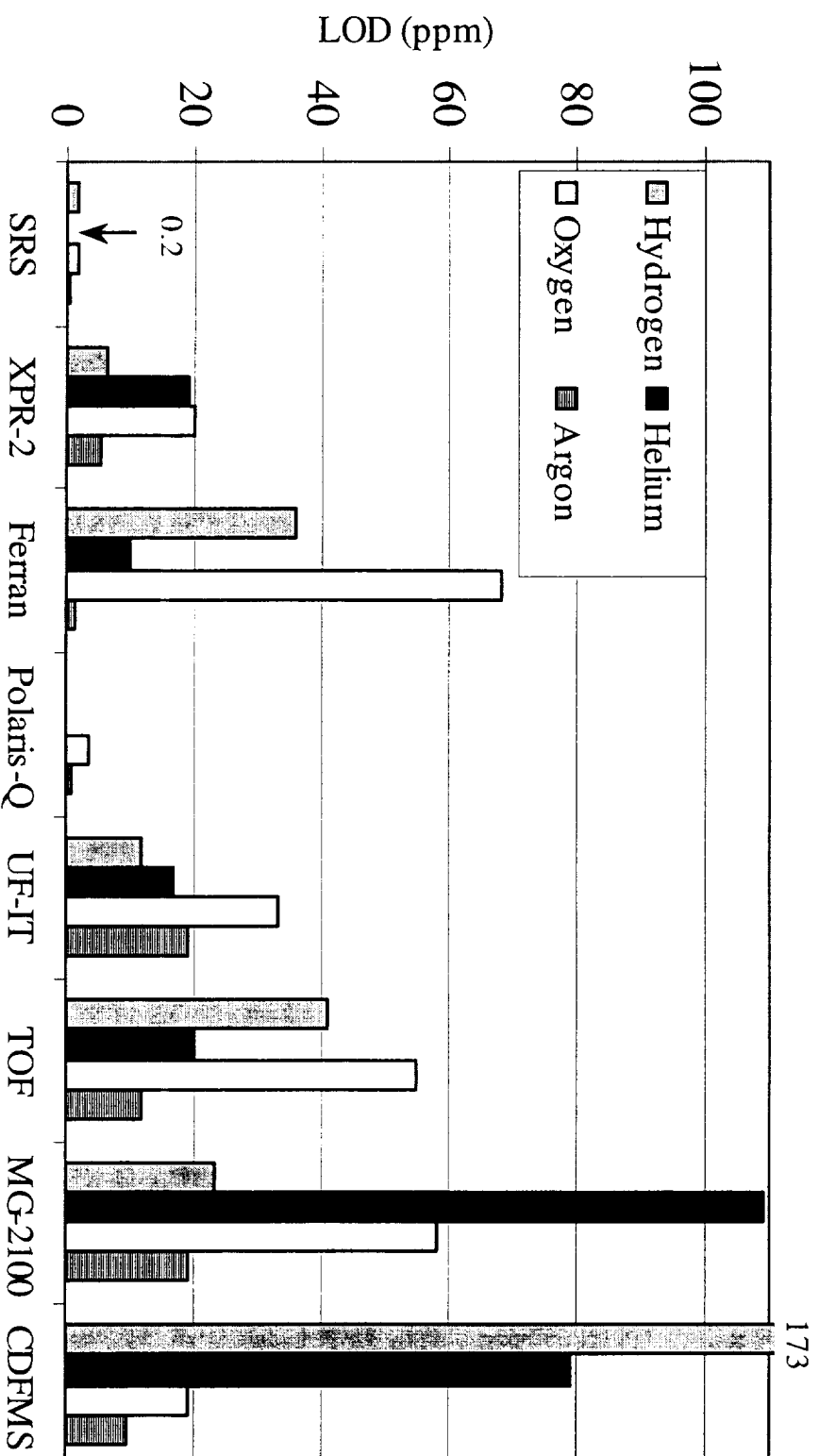
Figure 4  
Precision





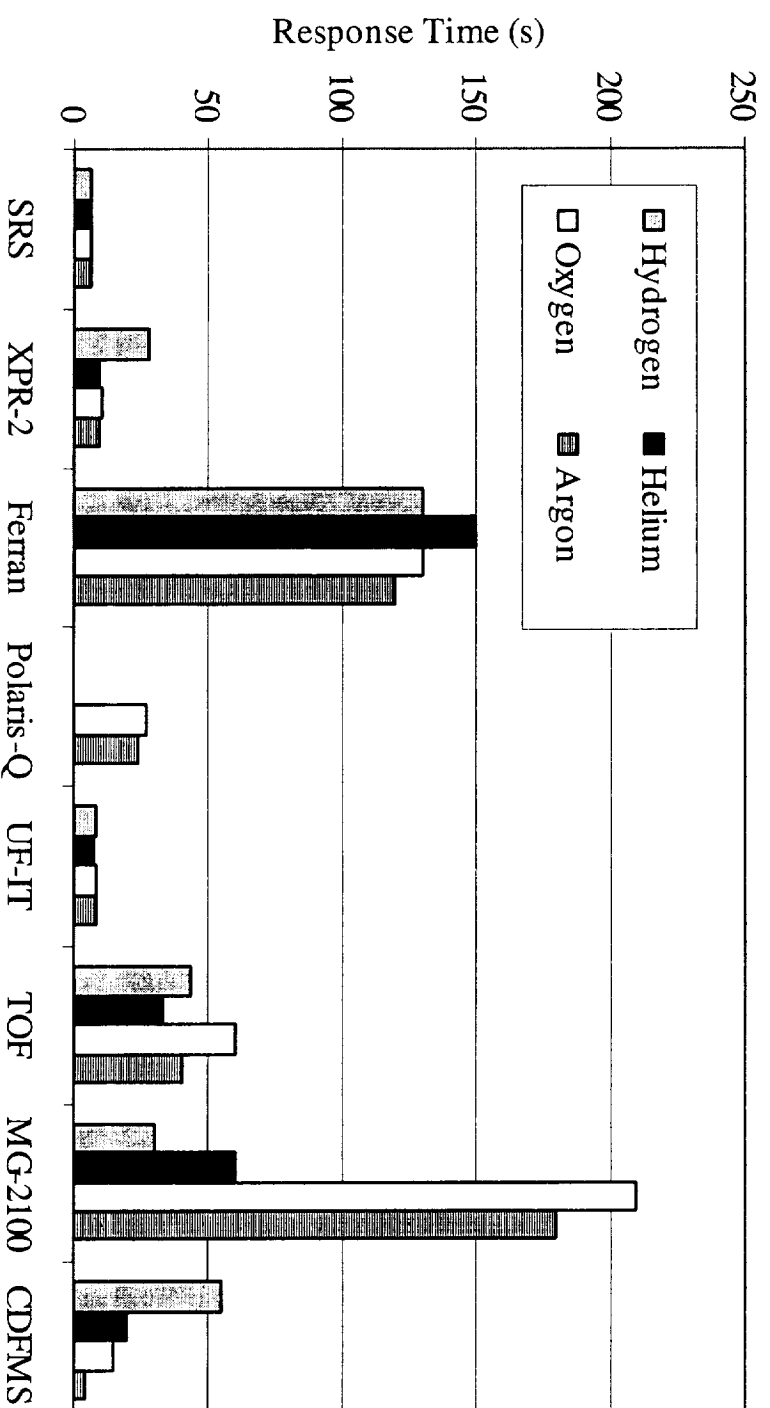
# Figure 5

## Limit of Detection (LOD)



# Figure 6

## Response Time



# Figure 7

## Recovery Time

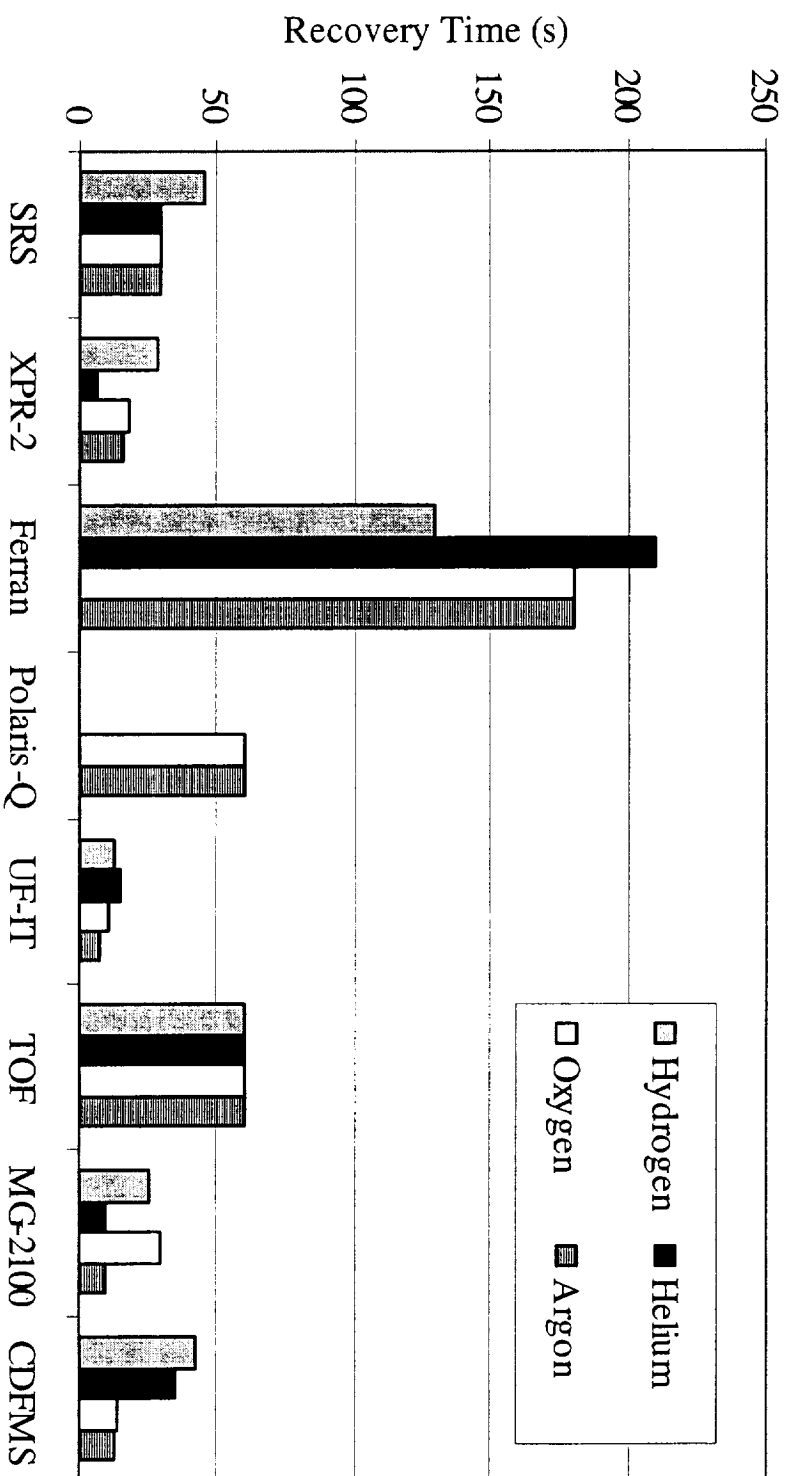
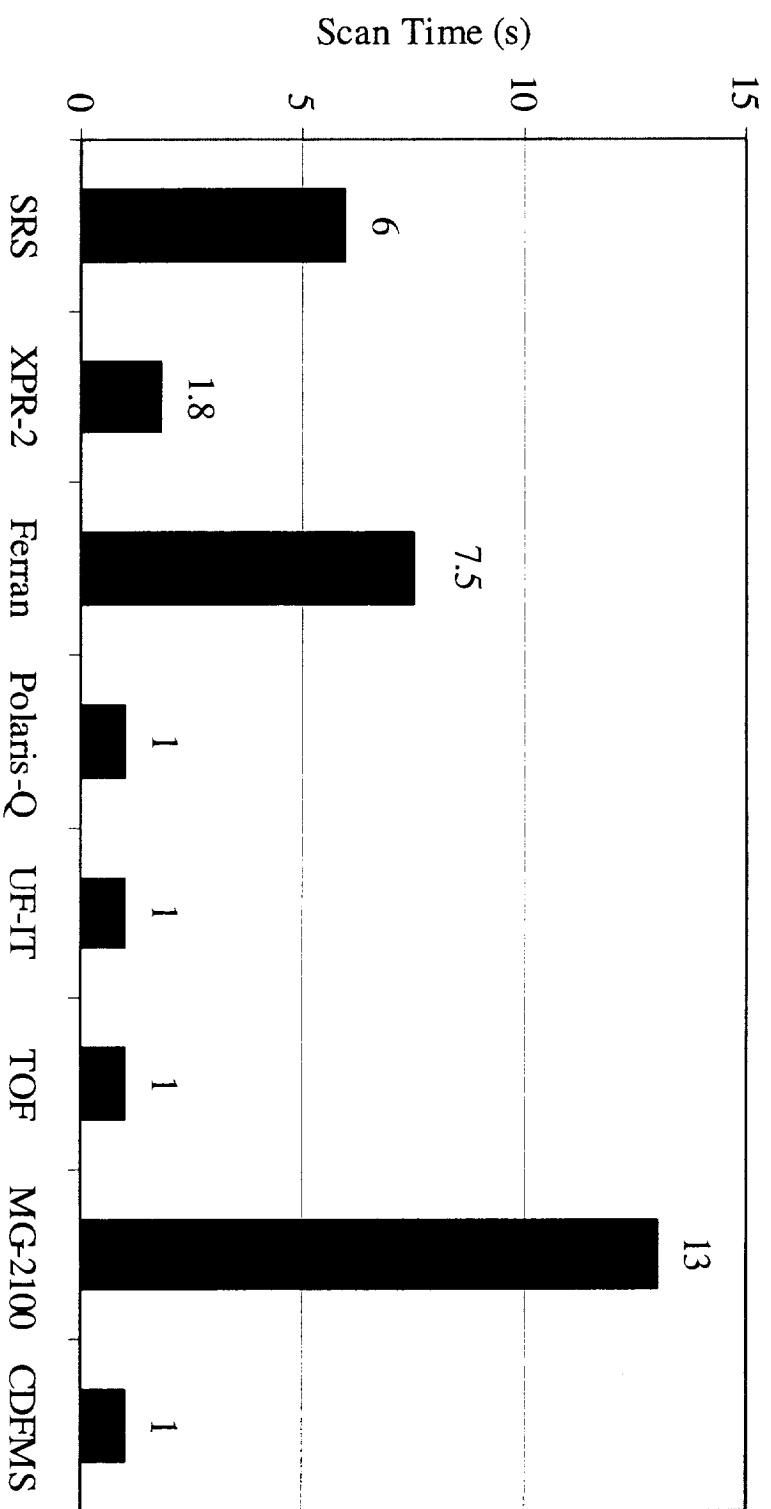
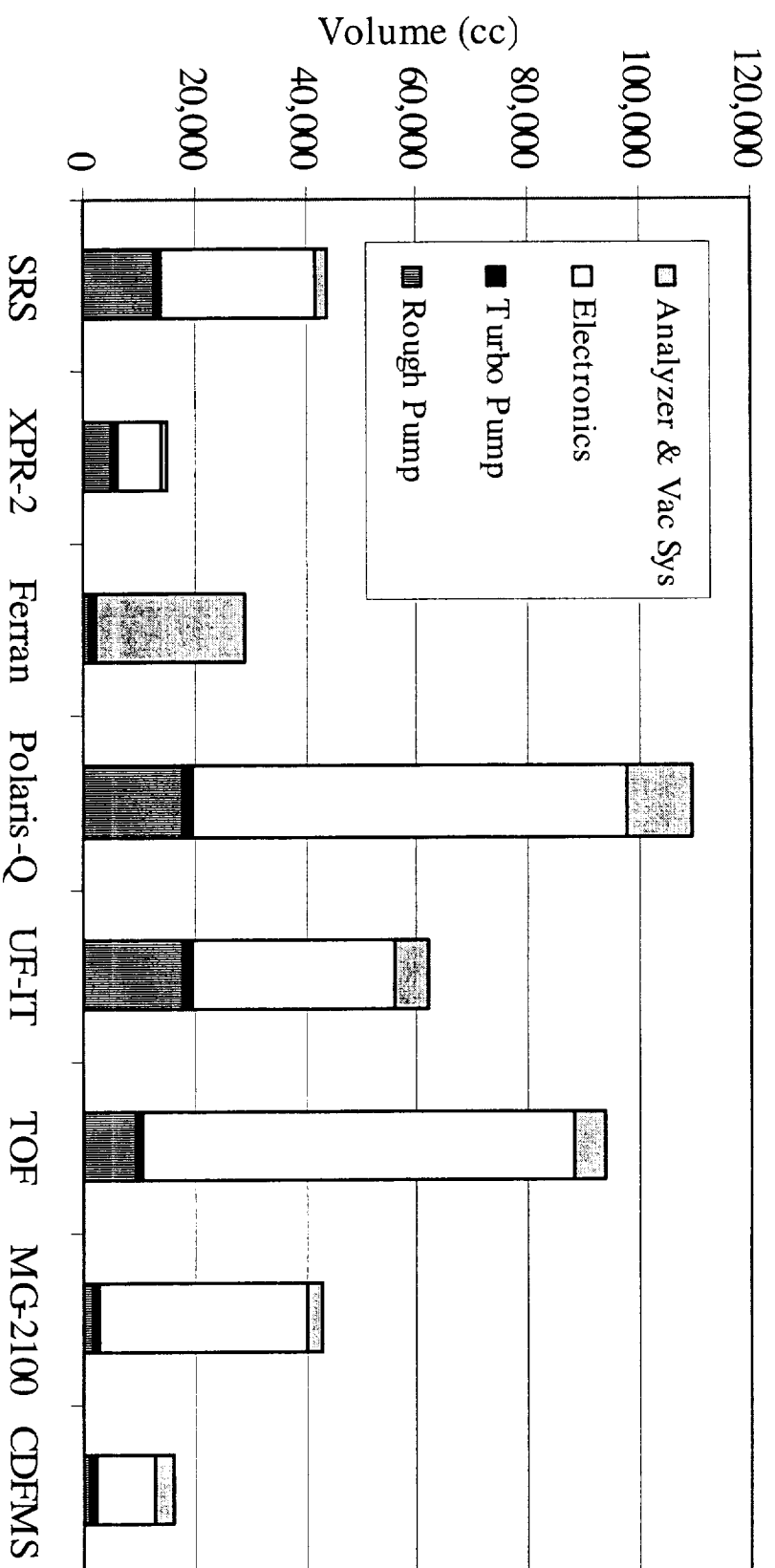


Figure 8  
Scan Time



# Figure 9

## System Volume



# Figure 10

## System Weight

